Treatment of Swimming Pool Water with UV Followed by Ozone

Cheema, Waqas Akram; Kaarsholm, Kamilla Marie Speht; Andersen, Henrik Rasmus

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

TREATMENT OF SWIMMING POOL WATER WITH UV FOLLOWED BY OZONE

Waqas A. Cheema[1, 2], Kamilla MS Hansen[1], Henrik R. Andersen[1]

[1]Department of Environmental Engineering, Technical University of Denmark, Miljøvej 113, 2800 Kongens Lyngby, Denmark

[2] National University of Sciences & Technology, H-12, Islamabad, Pakistan

Abstract

Both UV treatment and ozonation are used to reduce different types of disinfection byproducts (DBP) in swimming pools. UV treatment is most common as it is particularly efficient in removing the repulsive chlorine like smelling chloramines (combined chlorine). UV treatment of pool water increased the chlorine reactivity and formation of chloro-organic DBP such as trihalomethanes. Based on the similar selective reactivity of ozone and chlorine we hypothesized that the created reactivity towards chlorine by UV treatment of dissolved organic matter in pool water might also be expressed as an increased reactivity towards ozone and that ozonation might saturate the chlorine reactivity created by UV treatment and mitigate the increased DBP formation. We found that UV treatment makes pool water highly reactive to ozone. The created reactivity towards chlorine decreases dose dependently with ozone dosage prior to contact with chlorine. Furthermore, the kinetics of ozone in UV treated pool water changed drastically from a half-life in excess of 20 min to complete consumption in less than 2 min. Ozonation in UV treated pool water induced formation of some DBPs that are not commonly reported in pool water where trichloronitromethane is noteworthy as it is genotoxic however this created genotoxicity was removed by UV treatments when repeated experiments of combined UV/ozone treatment interchanged with chlorination for 24h were conducted. The discovered reaction can form the basis for a new treatment method for swimming pools.

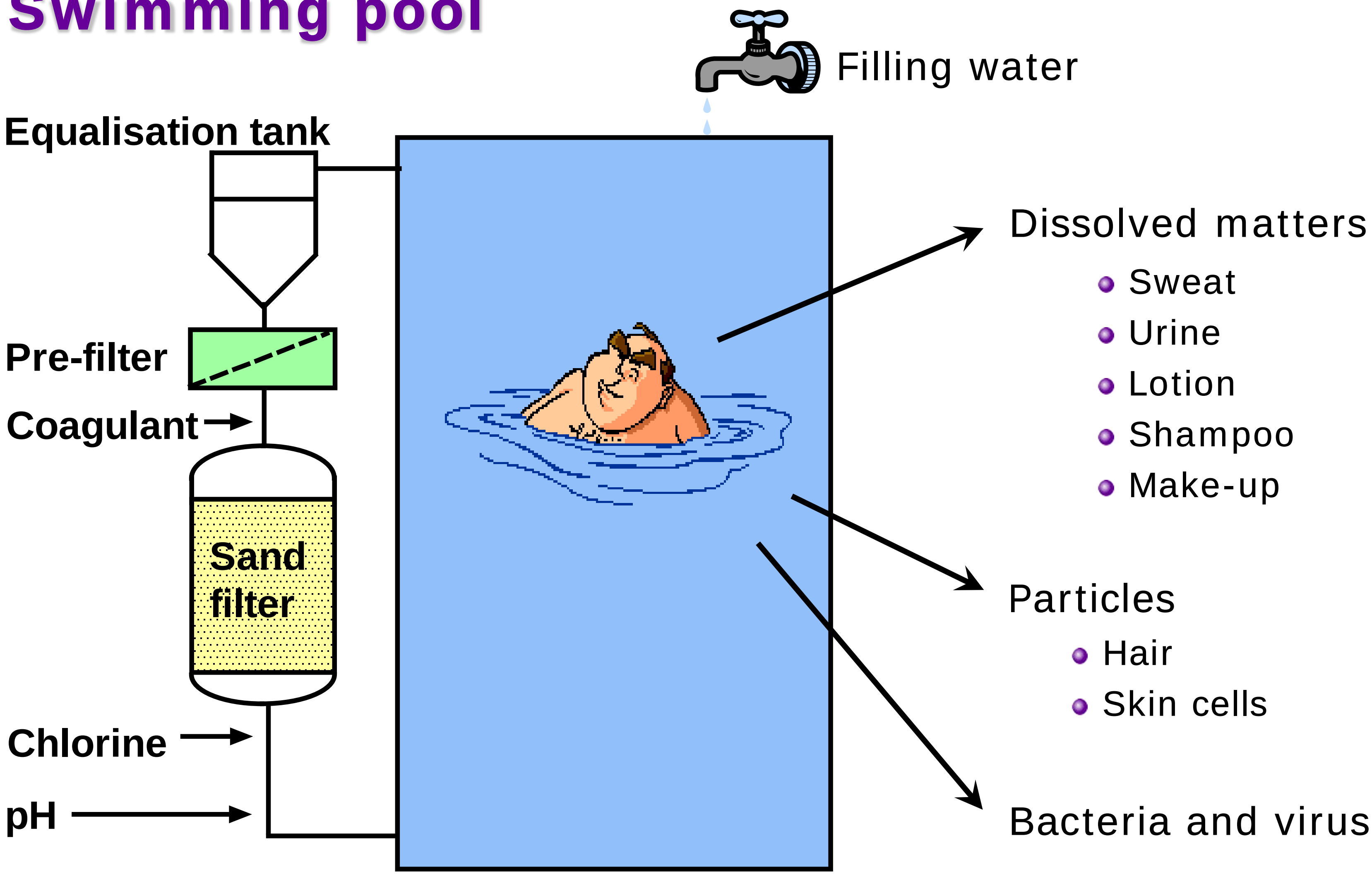
Treatment of swimming pool water with UV followed by ozone

W.A. Cheema, K.M.S. Hansen, H.R. Andersen

International Ozone Association (PAG-IOA) Conference
28 – 31 August, 2016
Las Vegas, Nevada

DTU Environment
Department of Environmental Engineering

Swimming pool



Disinfection byproducts (DBPs)

Chlorine

+

Dissolved matter

→

Byproducts

Trihalomethanes
Combined chlorine

Haloacetonitriles
Haloacetic acids
Trichloramine

⇓

Potential health risk

Ozone in pools

Oxidation of pollutants

I. Direct reaction

$$DOC + O_3 \rightarrow DOC_{\text{selectively oxidized}}$$

Fast consumption of ozone

Decrease chlorine reactivity of pollutants

Low ozone life time → no reaction with bromide

II. Radical reaction

$$H_2O + O_3 \rightarrow O_2 + 2\ HO^{\bullet}$$

$$DOC + HO^{\bullet} \rightarrow DOC_{\text{radical oxidized}}$$

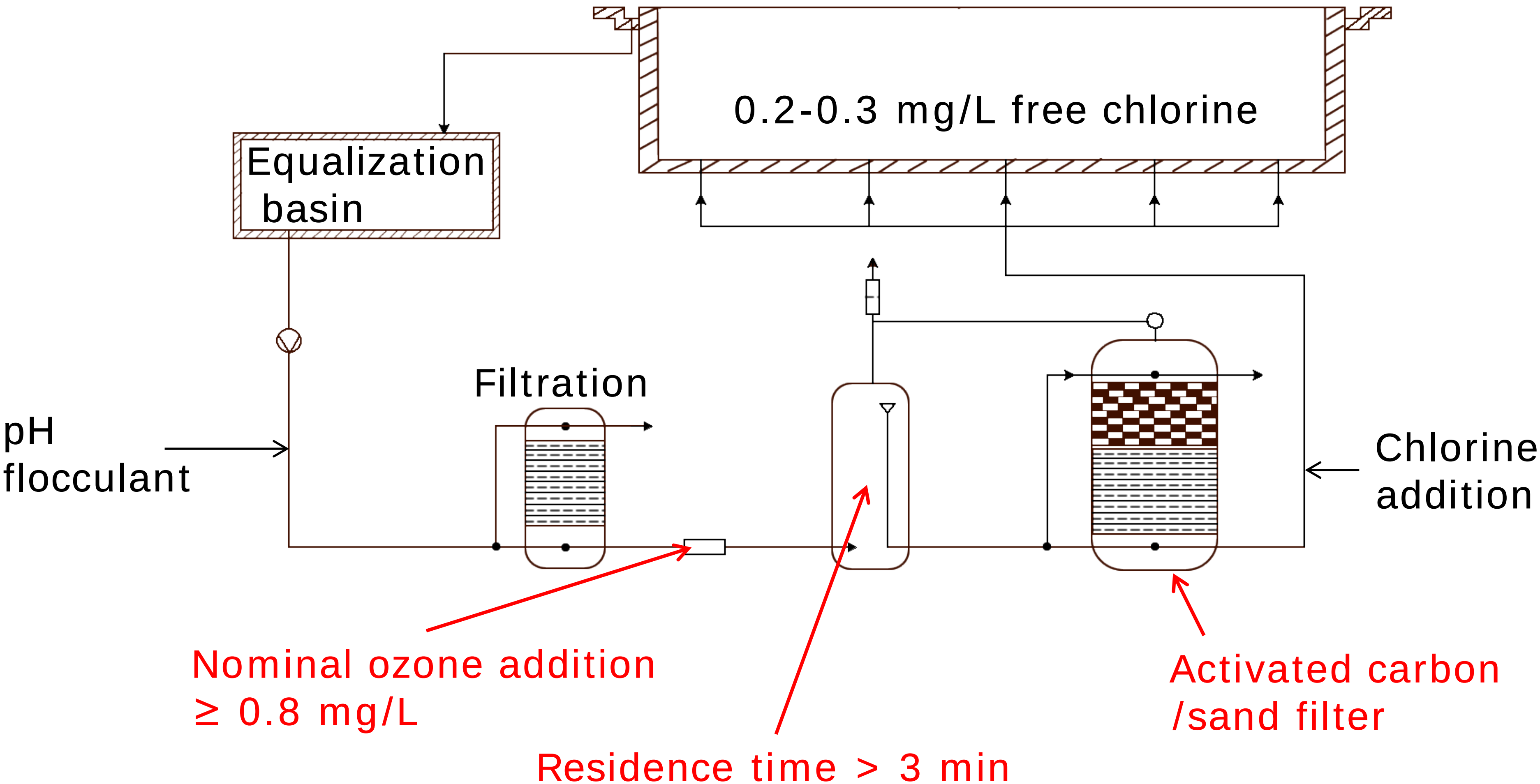
Slow consumption of ozone

Ozone converts to hydroxyl radicals with time

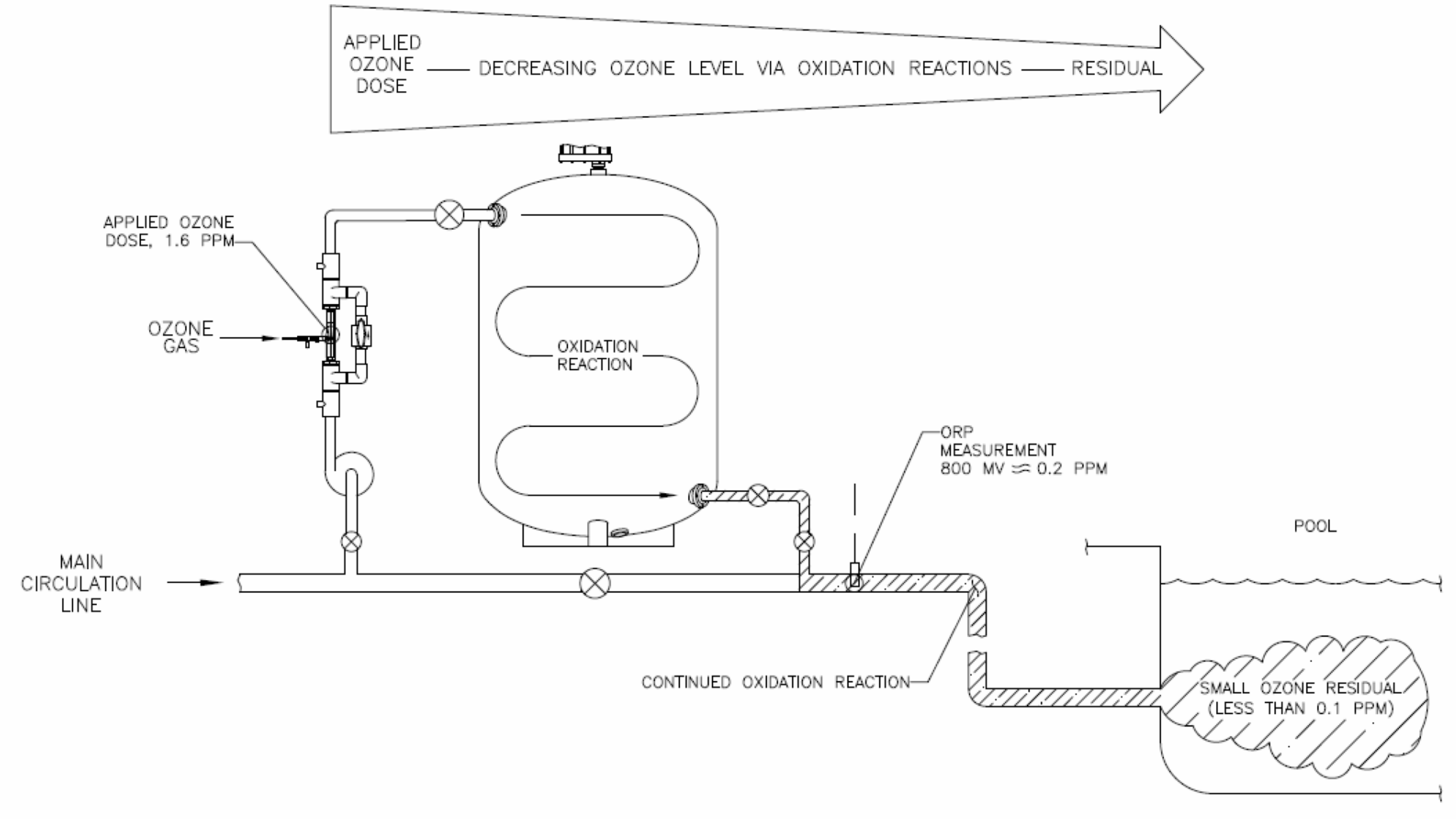
Radical attack of inactive carbon → increased chlorine reactivity

Long ozone life time → oxidation of bromide to bromate

Systems: DIN (German standard)

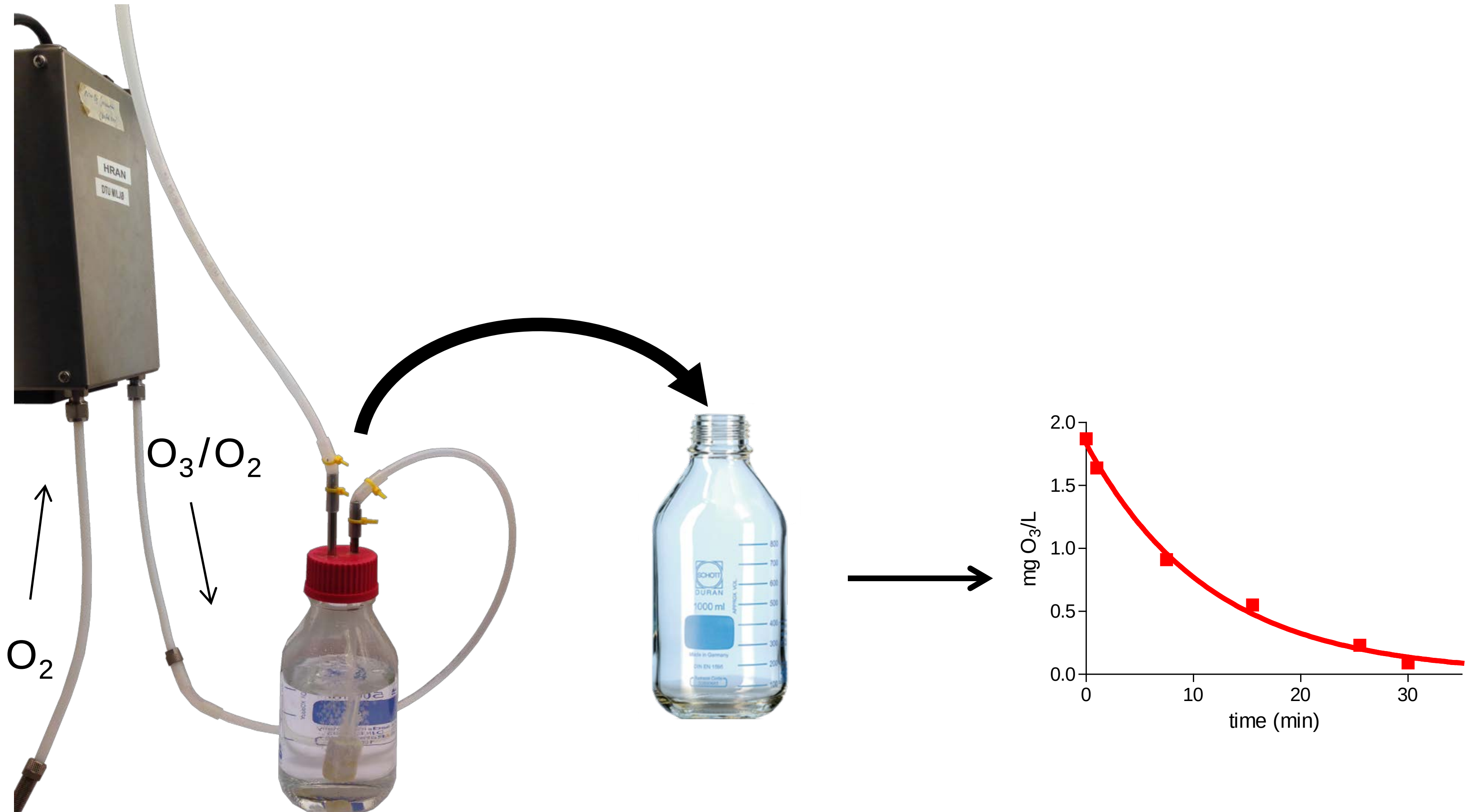


Systems: Slip-stream (USA)



DEL Ozone proprietary drawing

Lab-scale experiments



O_3 collection bottle

Chlorination of the ozonated samples

Chlorine: 24 h at 25 °C

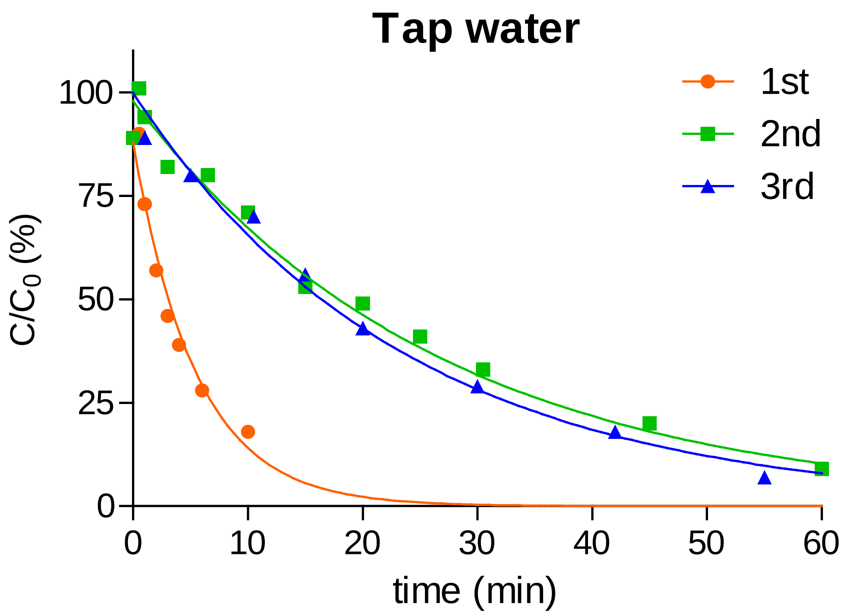
Chlorine residual
Aim: 1-3 mg/L

&

Trihalomethane by purge&trap – GC/MS

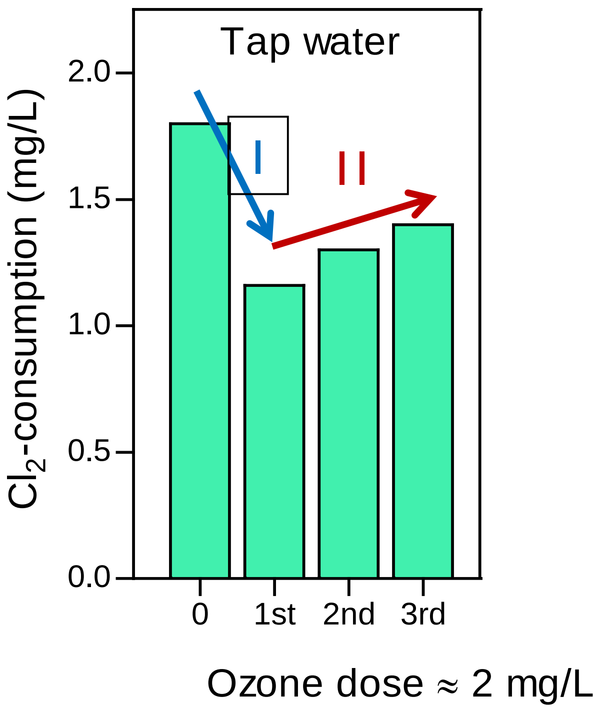
DTU Environm
Department of

Repeated ozonation – ozone lifetime



- Fast removal of 1st ozone dose → ozone reactive material
- 2nd and 3rd → no ozone reactive material

Chlorine consumption

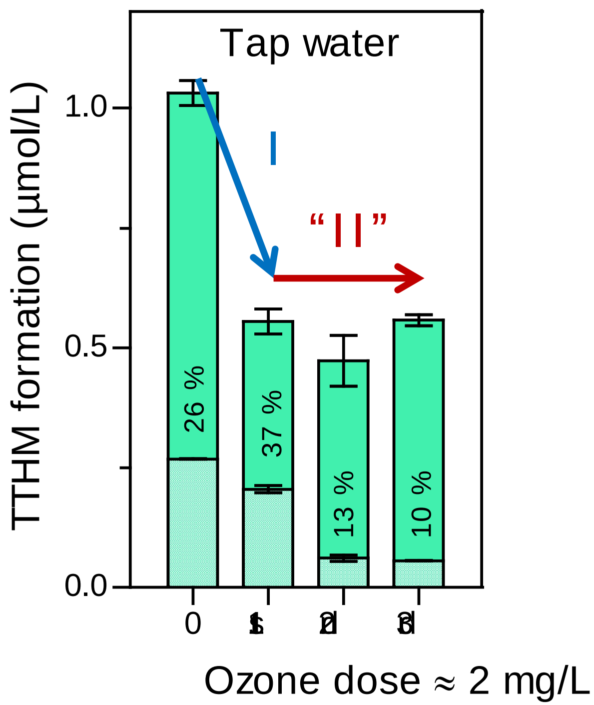


I. Direct oxidation by ozone

II. Radical mechanism

- Different chlorine consumption for tap water and swimming pool water

Formation of total trihalomethane

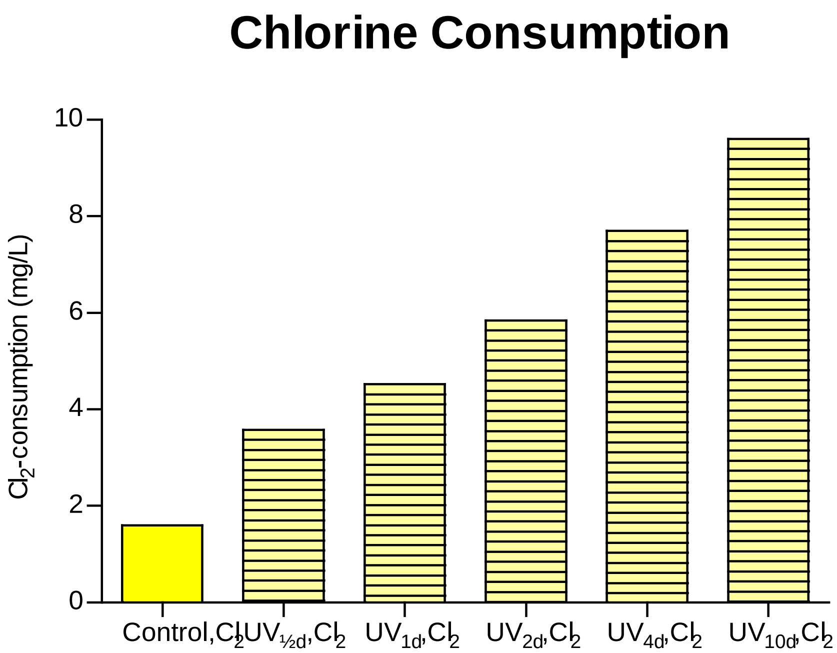


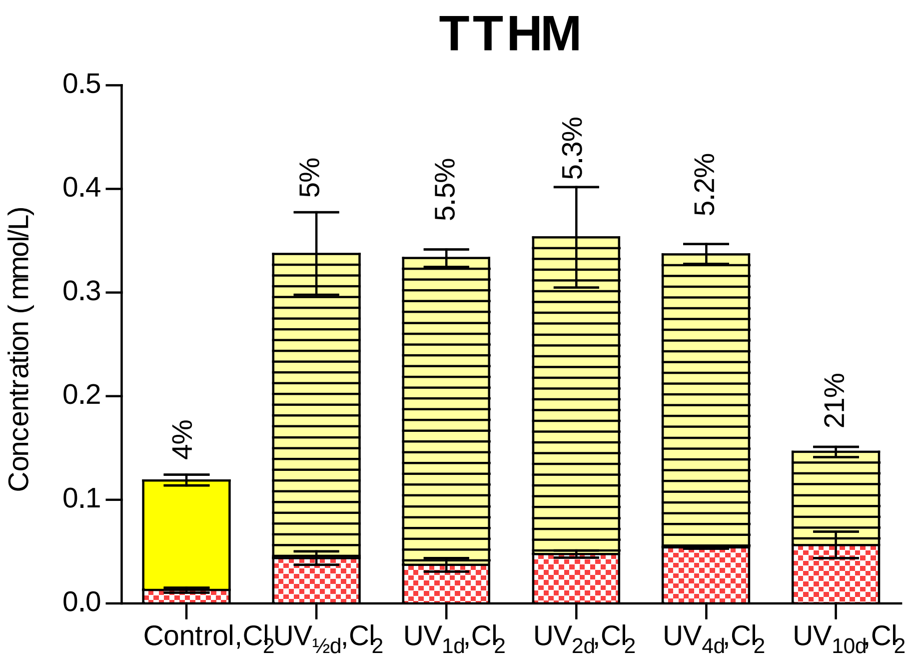
I. Direct oxidation by ozone

II. Radical mechanism

- Ozonation of tap water → decreased THM
- Ozonation of pool water → increased THM

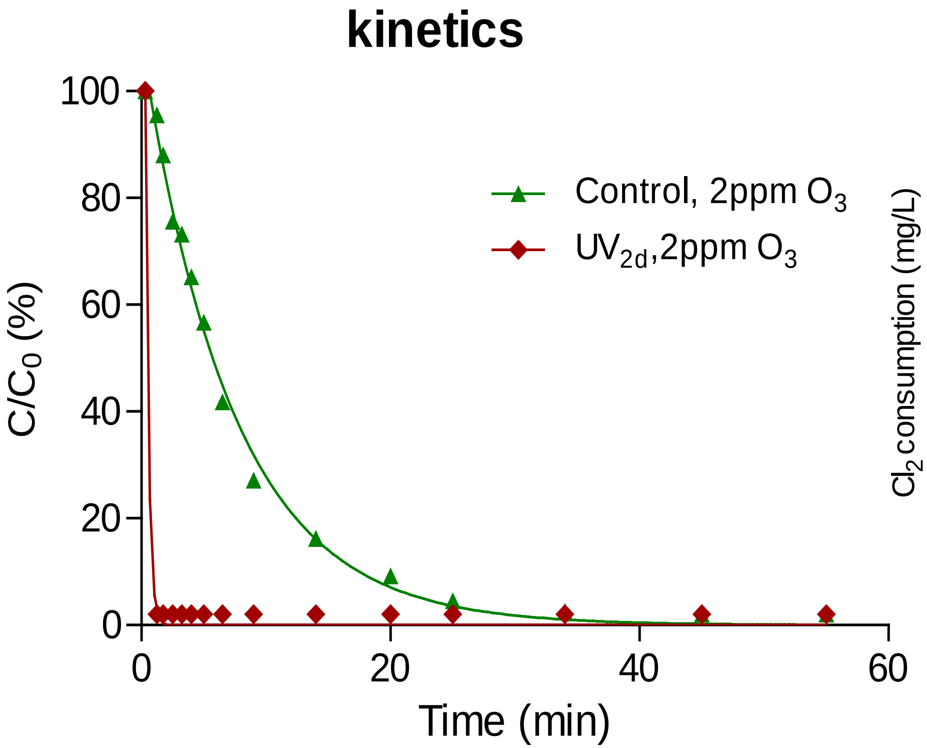
Range finding for the effect of UV activation on chlorine reaction

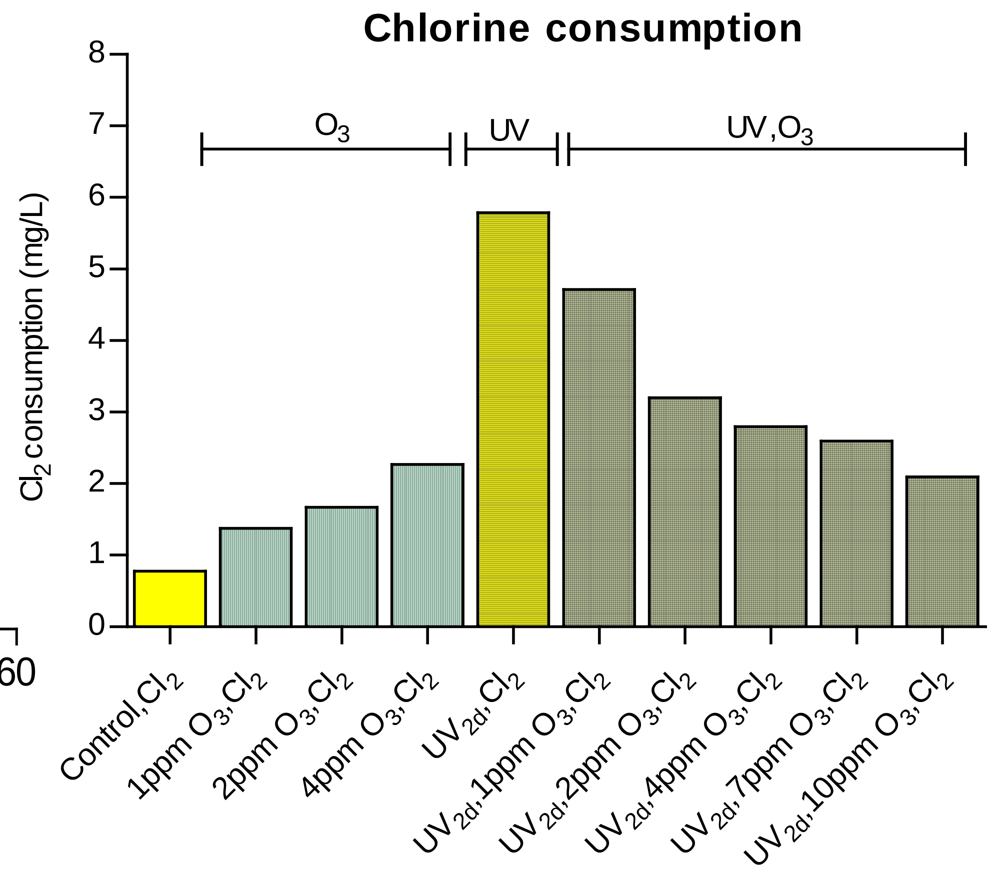




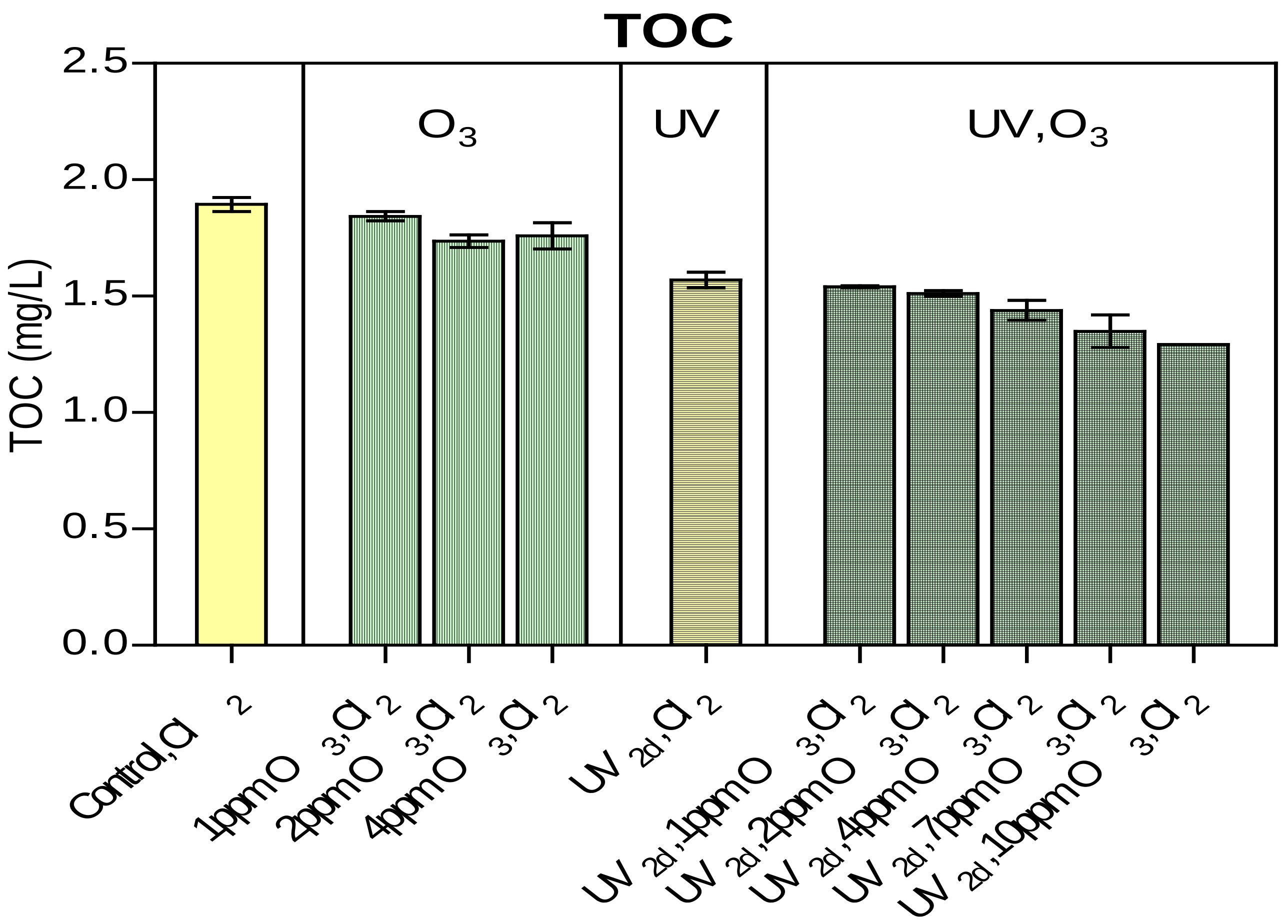
DTU Environment
Department of Environmental Engineering

Ozone kinetics and chlorine consumption



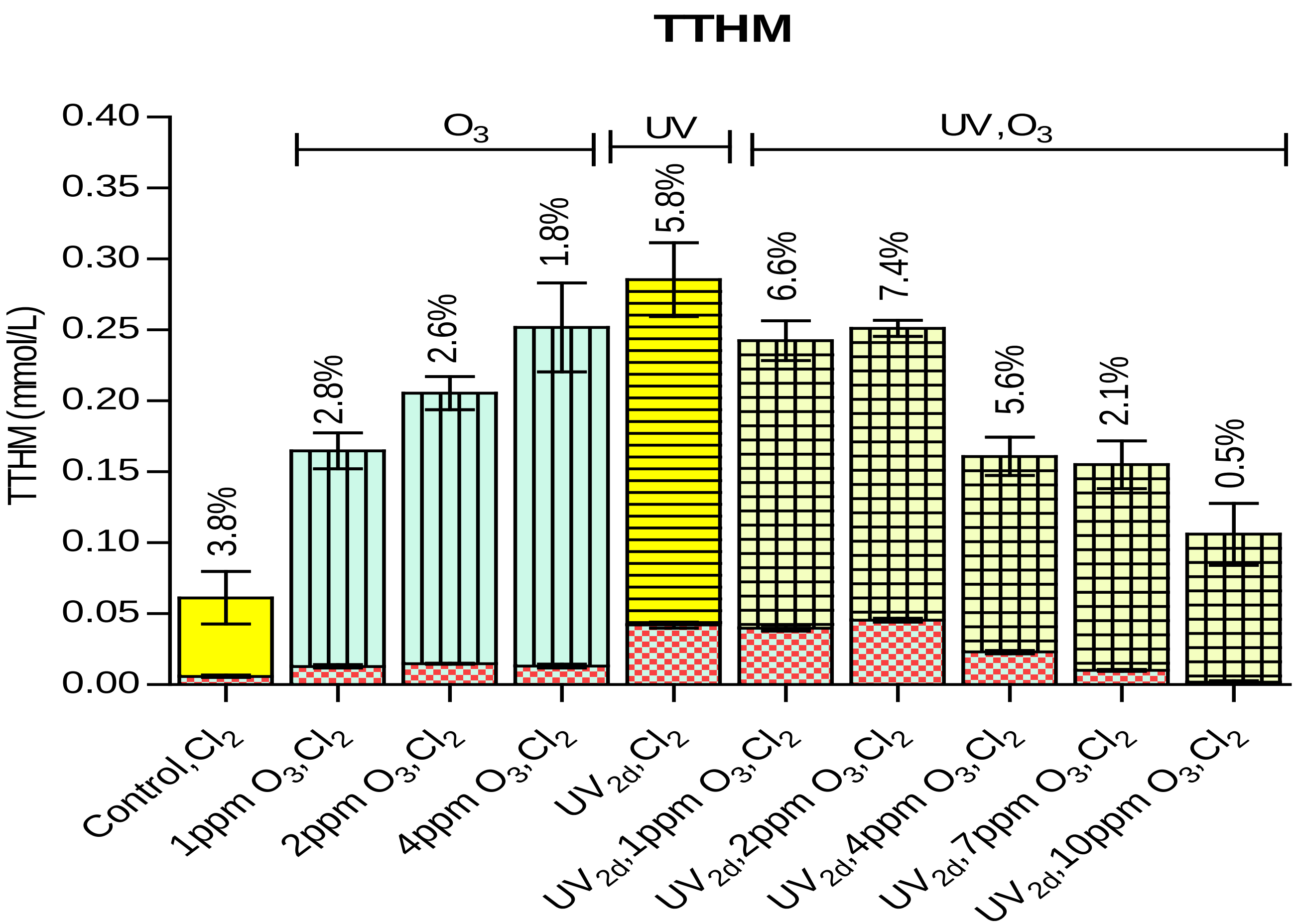


Dissolved organic carbon at different experimental treatment



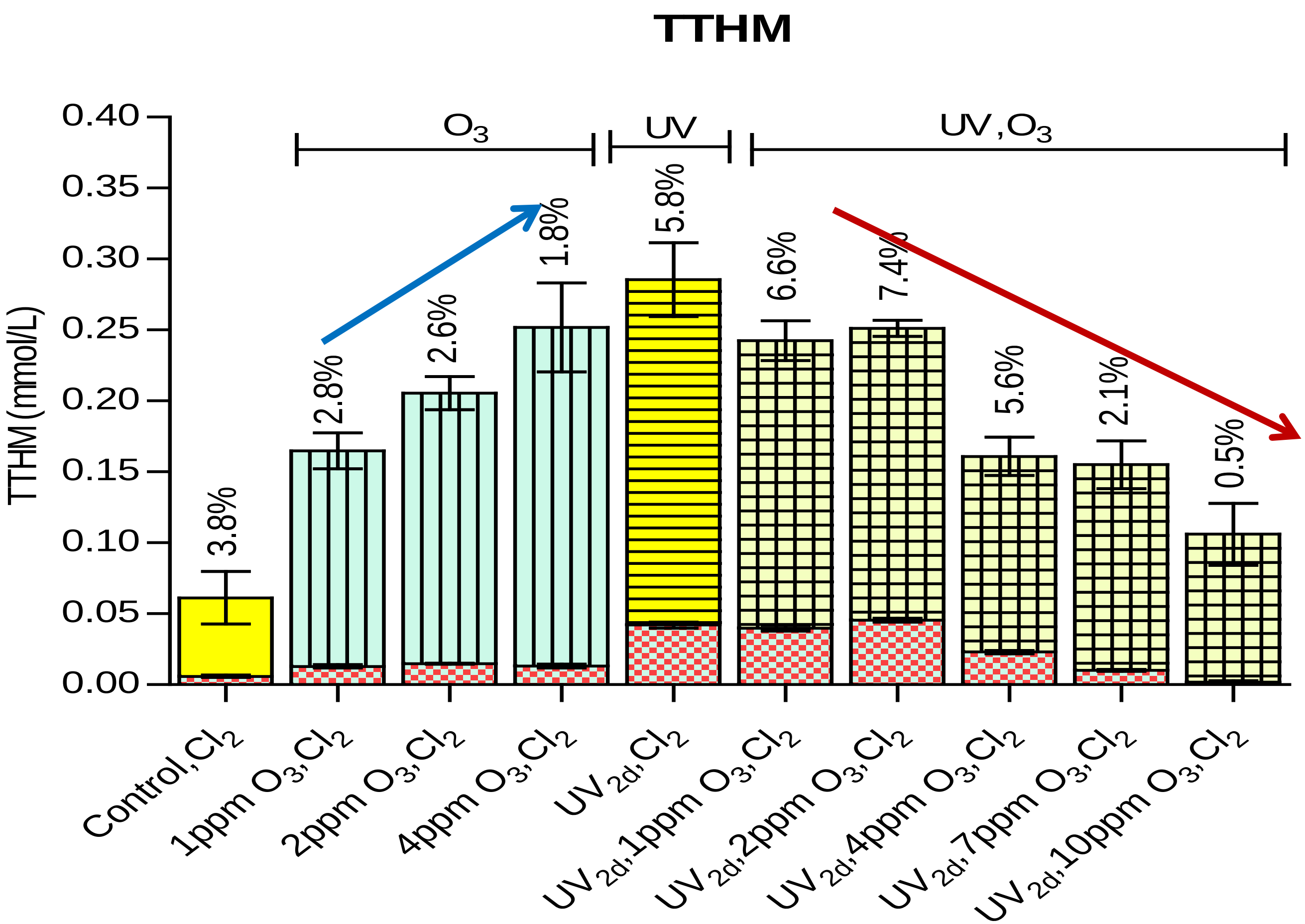
DTU Environment
Department of Environmental Engineering

Trihalomethanes

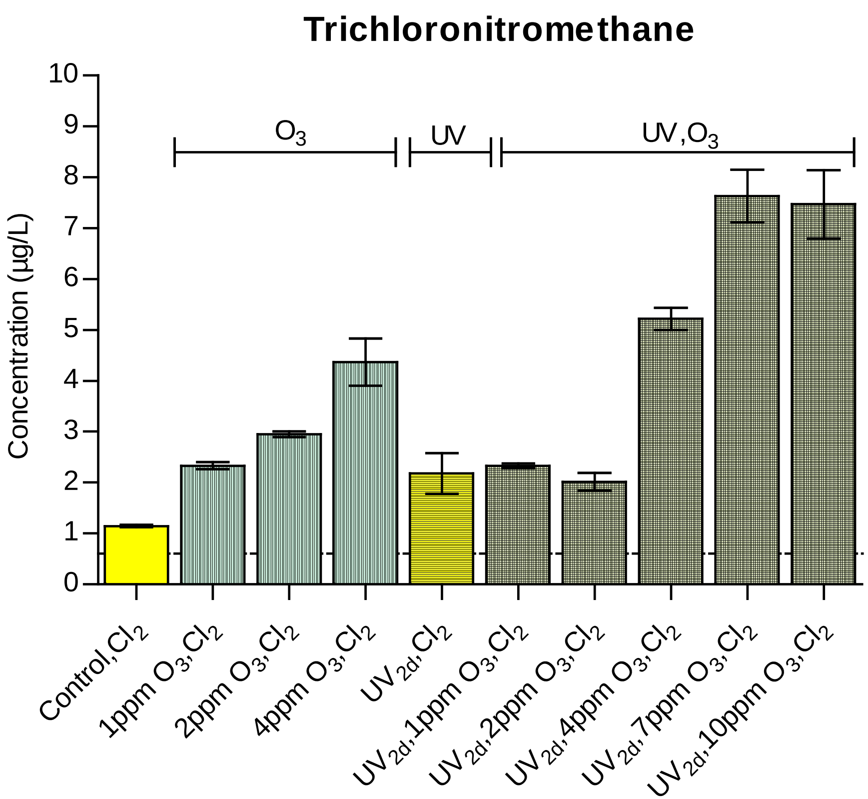


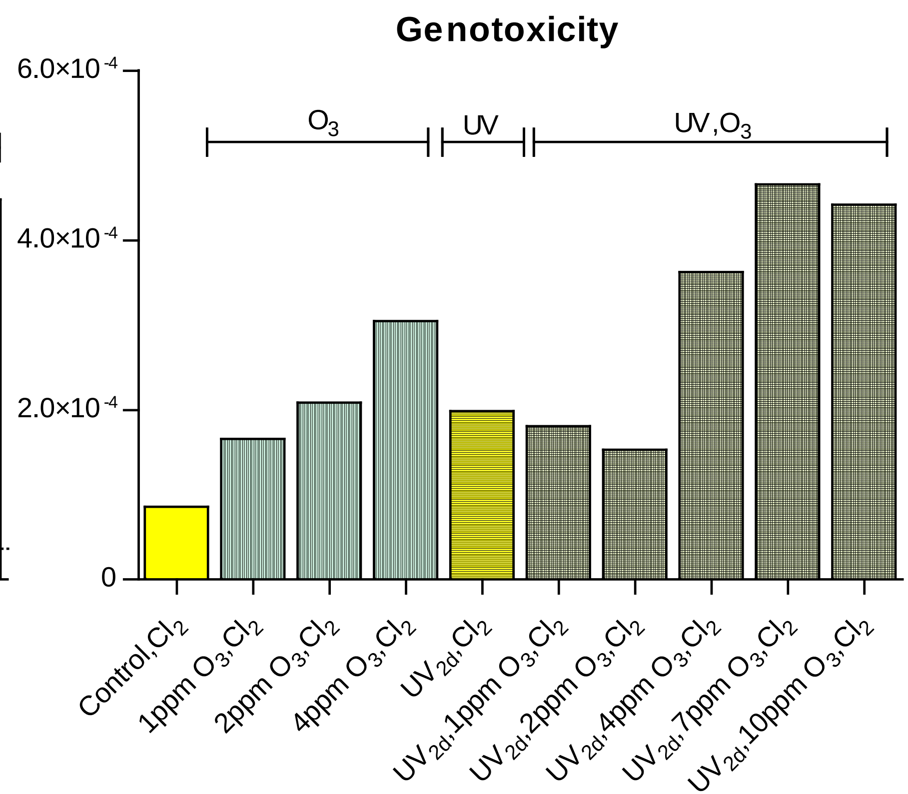
DTU Environment
Department of Environmental Engineering

Trihalomethanes



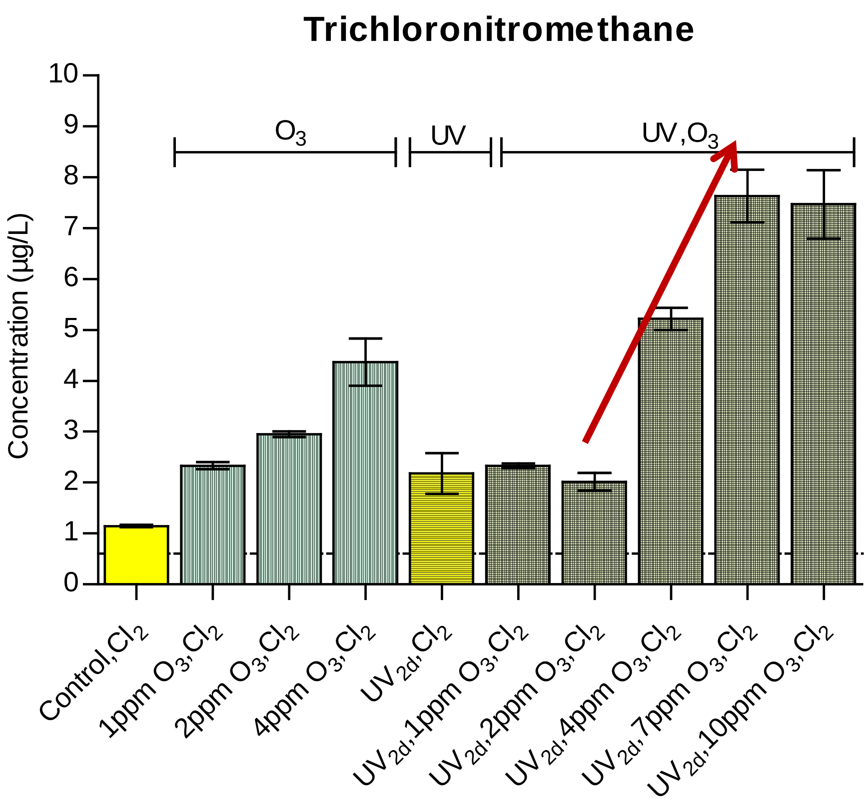
Toxicity



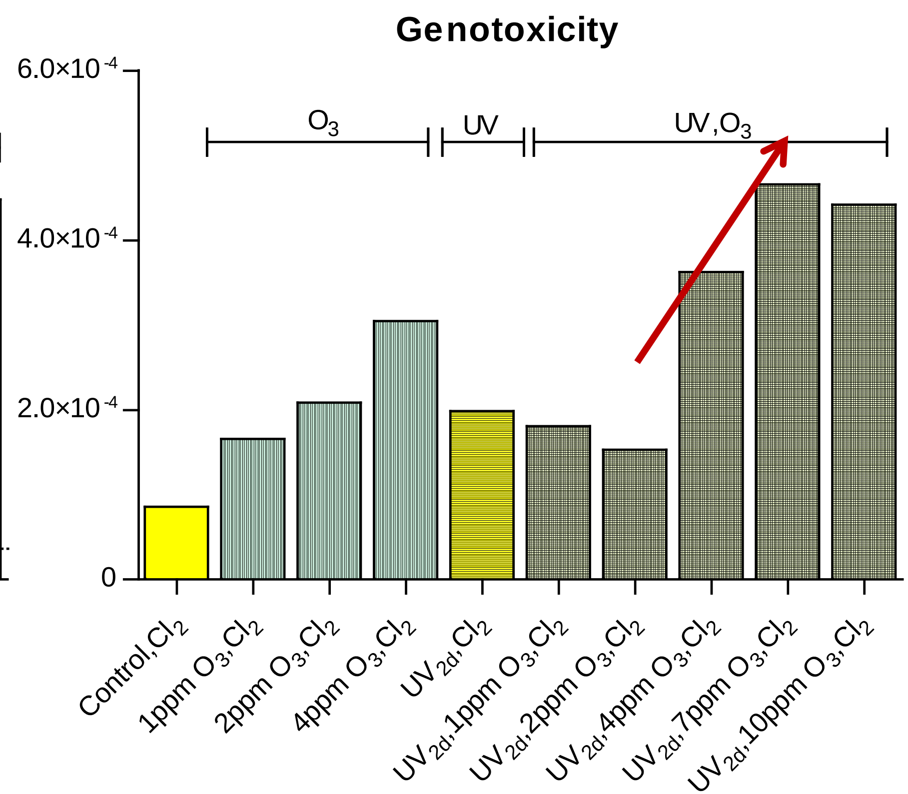


DTU Environment
Department of Environmental Engineering

Toxicity

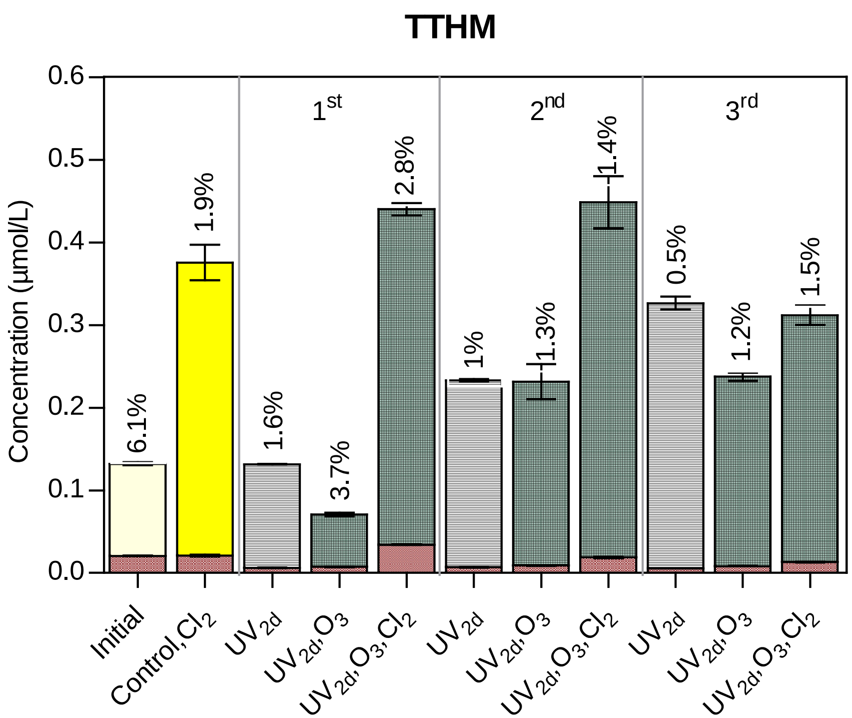


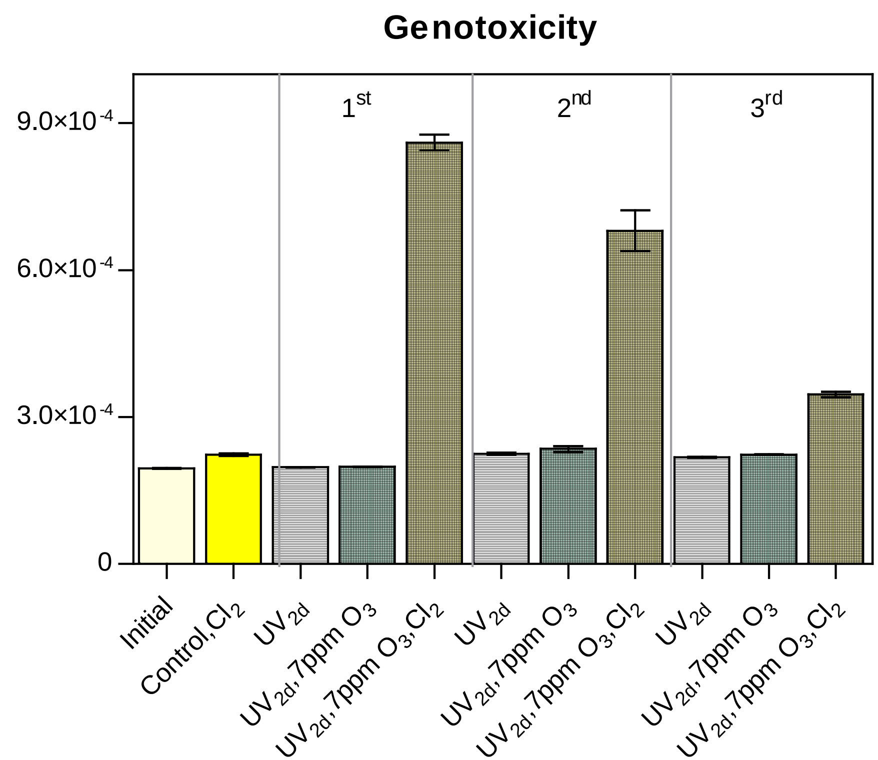
Trichloronitromethane
Concentration (µg/L)
10
9
8
7
6
5
4
3
2
1
0
O3
UV
UV,O3
Control,Cl2
1ppm O3,Cl2
2ppm O3,Cl2
4ppm O3,Cl2
UV2d,Cl2
UV2d,1ppm O3,Cl2
UV2d,2ppm O3,Cl2
UV2d,4ppm O3,Cl2
UV2d,7ppm O3,Cl2
UV2d,10ppm O3,Cl2



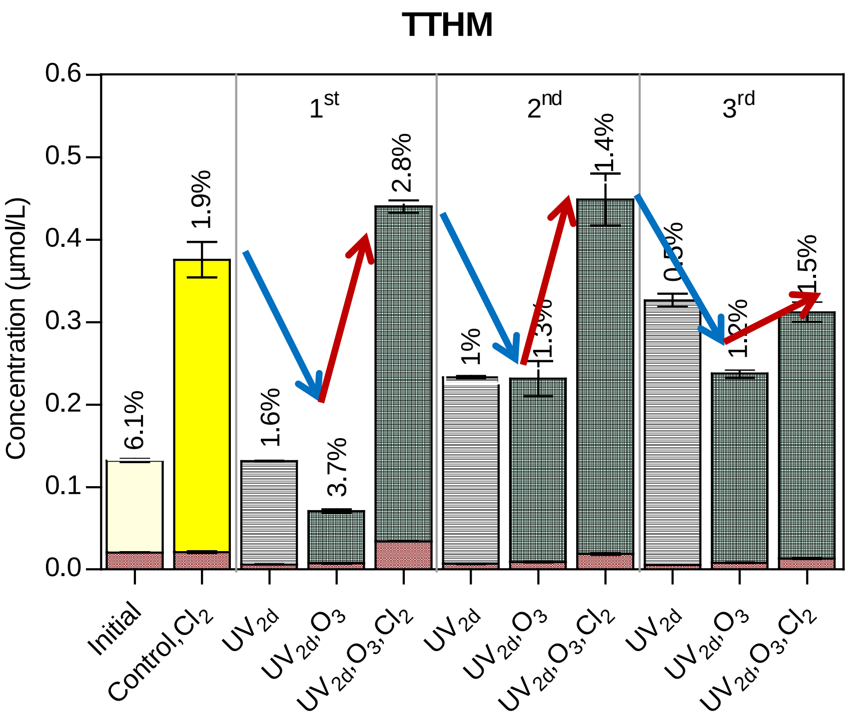
Genotoxicity
6.0×10-4
4.0×10-4
2.0×10-4
0
O3
UV
UV,O3
Control,Cl2
1ppm O3,Cl2
2ppm O3,Cl2
4ppm O3,Cl2
UV2d,Cl2
UV2d,1ppm O3,Cl2
UV2d,2ppm O3,Cl2
UV2d,4ppm O3,Cl2
UV2d,7ppm O3,Cl2
UV2d,10ppm O3,Cl2

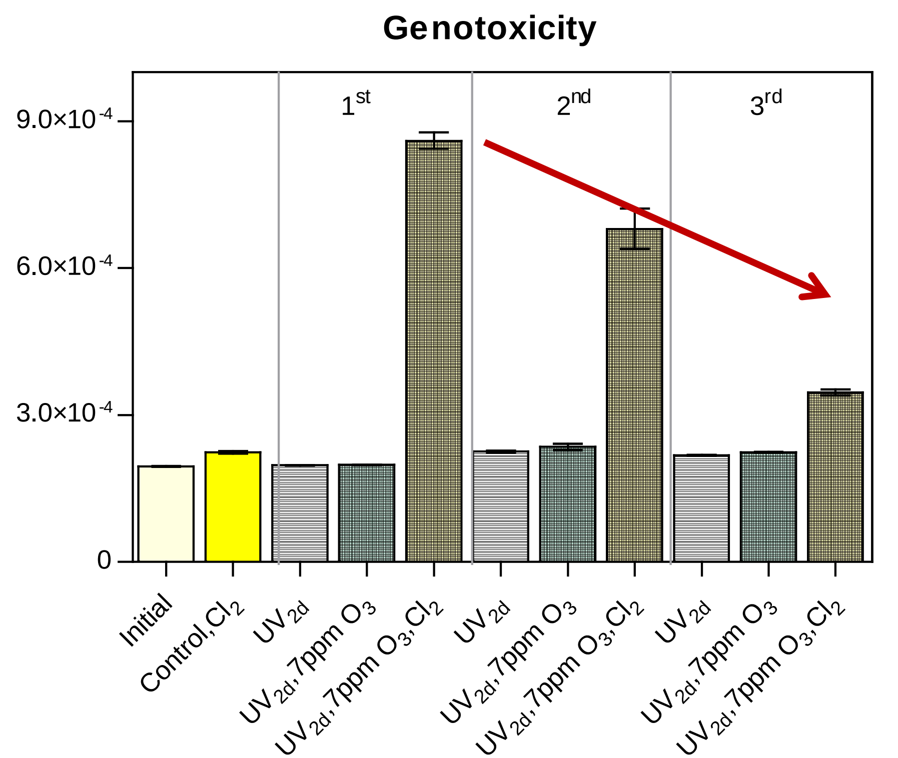
Repeated treatment cycle



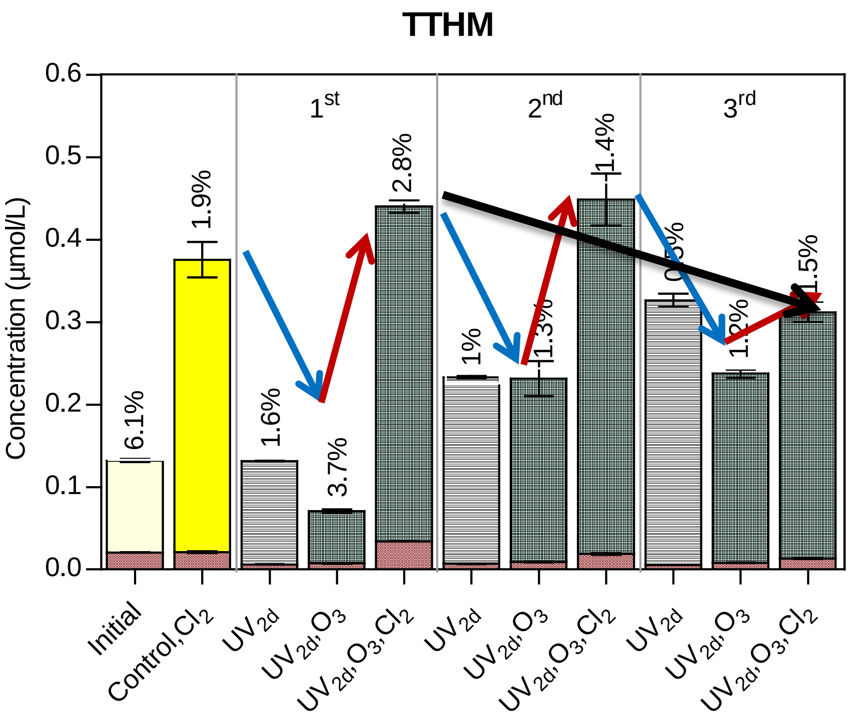


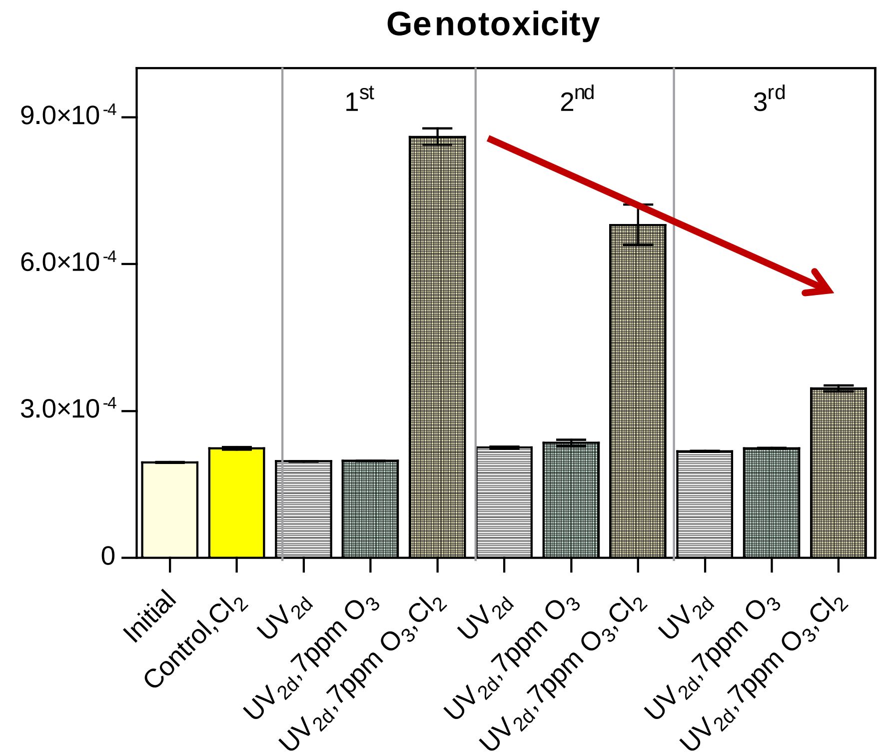
Repeated treatment cycle





Repeated treatment cycle





Effect of ozone and UV on the formation of DPB during chlorination

DBP	DBP formation during chlorination after treatment		Effect on the DBPs themselves	
	Increase	Decrease	Increase	Decrease
Dichloroacetonitrile	UV, O_3	O_3	UV*	O_3
Bromochloroacetonitrile	UV, O_3	O_3	-	UV
Chloroform	UV, O_3	O_3	-	-
Bromodichloromethane	UV, O_3	O_3	-	UV
Dibromochloromethane	UV, O_3	O_3	-	UV
Dichloropropanone	UV, O_3	O_3	UV*	O_3
Trichloropropanone	UV, O_3	-	-	UV
Trichloronitromethane	UV, O_3	-	-	UV

* Confirmed in Spiliotopoulou et al. (2015)

Summary

- UV treatment increased the reactivity of pool water to both chlorine and ozone
- Ozonation of UV-treated water decreased chlorine reaction and by-product formation
- Genotoxic trichloronitromethane formed by ozonation was removed with UV treatment
- Combined UV-ozone treatment decreases chlorine by-product formation
- UV-ozone treatment is predicted to improve swimming pool water quality

Thanks for your attention!

Waqas Cheema
PhD Fellow
wche@env.dtu.dk